# Supplementary Materials: Coinage Metal Complexes of the Carbenic Tautomer of a Conjugated Mesomeric Betaine Akin to Nitron

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**X-ray crystallography:**



**DFT calculations:**



**Plots of NMR spectra:**

**Table S1.** Data collection and structure refinement details.

| | **6**H[$BF_4$] | **6** | **6'=S** | [RhCl(**6'**)(COD)]] | [RhI(**6'**)(COD)]] | [CuCl(**6'**)]·$CH_2Cl_2$ | [AuCl(**6'**)] | [CuCl(**6'**)$_2$] | [CuBr(**6'**)$_2$] | [AgBr(**6'**)$_2$]·$C_7H_8$ | [Ag(**6'**)$_2$]Br | [Ag(**6'**)$_2$](OTf) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Chem. formula | $C_{11}H_{23}BF_4N_4$ | $C_{11}H_{22}N_4$ | $C_{11}H_{22}N_4S$ | $C_{19}H_{34}ClN_4Rh$ | $C_{19}H_{34}IN_4Rh$ | $C_{23}H_{46}Cl_4Cu_2N_8$ | $C_{11}H_{22}AuClN_4$ | $C_{22}H_{44}ClCuN_8$ | $C_{22}H_{44}BrCuN_8$ | $C_{29}H_{52}AgBrN_8$ | $C_{22}H_{44}AgBrN_8$ | $C_{23}H_{44}AgF_3N_8O_3S$ |
| Formula mass | 298.14 | 210.32 | 242.38 | 456.86 | 548.31 | 703.56 | 442.74 | 519.64 | 564.10 | 700.56 | 608.43 | 677.59 |
| Crystal system | orthorhombic | monoclinic | monoclinic | monoclinic | monoclinic | triclinic | monoclinic | orthorhombic | orthorhombic | monoclinic | orthorhombic | triclinic |
| Space group | *P b c a* | *I a* | *C* 2/*c* | *P* $2_1$/*c* | *P* $2_1$/*c* | *P* −1 | *C* 2/*c* | *P b c n* | *P b c n* | *P* $2_1$/*n* | *C* 2 2 $2_1$ | *P* 1 |
| *a*/Å | 10.3118(3) | 9.5203(5) | 22.431(2) | 13.2122(4) | 13.5955(4) | 10.3279(6) | 15.3460(9) | 10.9369(6) | 10.8319(7) | 14.7525(7) | 9.3230(8) | 8.2561(9) |
| *b*/Å | 26.4187(10) | 11.1150(5) | 11.3451(6) | 26.5736(9) | 27.3237(10) | 14.0466(8) | 20.7976(9) | 10.0225(6) | 9.9667(6) | 13.3286(4) | 14.0077(9) | 8.1726(9) |
| *c*/Å | 11.3460(3) | 11.7903(7) | 11.3470(9) | 12.1591(4) | 12.1111(4) | 13.9264(7) | 11.7713(6) | 24.9910(16) | 24.815(2) | 17.2248(7) | 22.283(2) | 12.9281(14) |
| *α*/° | 90 | 90 | 90 | 90 | 90 | 65.343(4) | 90 | 90 | 90 | 90 | 90 | 99.363(8) |
| *β*/° | 90 | 90.563(4) | 101.364(6) | 103.994(3) | 104.372(2) | 84.903(5) | 109.632(4) | 90 | 90 | 95.498(4) | 90 | 100.770(8) |
| *γ*/° | 90 | 90 | 90 | 90 | 90 | 73.737(5) | 90 | 90 | 90 | 90 | 90 | 112.147(8) |
| *V*/Å$^3$ | 3090.9(2) | 1247.57(11) | 2831.0(4) | 4142.3(2) | 4358.2(3) | 1761.7(2) | 3538.5(3) | 2739.4(3) | 2679.0(3) | 3371.3(2) | 2910.0(4) | 767.22(15) |
| *T*/K | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal size/mm | 0.55×0.32×0.08 | 0.15×0.15×0.05 | 0.32×0.09×0.02 | 0.19×0.17×0.07 | 0.27×0.17×0.08 | 0.23×0.04×0.02 | 0.03×0.03×0.02 | 0.41×0.24×0.04 | 0.18×0.14×0.02 | 0.18×0.17×0.12 | 0.25×0.17×0.05 | 0.30×0.05×0.05 |
| *Z* | 8 | 4 | 8 | 8 | 8 | 2 | 8 | 4 | 4 | 4 | 4 | 1 |
| $\mu$/mm$^{-1}$ | 0.112 | 0.544 | 0.212 | 0.963 | 2.210 | 1.535 | 8.455 | 0.919 | 2.332 | 1.813 | 2.089 | 0.781 |
| No. of refls measured | 23156 | 7774 | 6619 | 21672 | 27319 | 12584 | 7888 | 9413 | 6739 | 15506 | 12905 | 16235 |
| Indep. refls | 4668 | 1983 | 2631 | 7869 | 10239 | 6505 | 3241 | 2684 | 2484 | 6260 | 3501 | 5475 |
| [$R_{int}$] | [0.0202] | [0.0109] | [0.0596] | [0.0364] | [0.0357] | [0.0434] | [0.0286] | [0.0409] | [0.0383] | [0.0608] | [0.0357] | [0.0316] |
| Final $R_1$ ($wR_2$) [$I > 2\sigma(I)$] | 0.0382 (0.0885) | 0.0250 (0.0637) | 0.0689 (0.1853) | 0.0580 (0.1593) | 0.0457 (0.1240) | 0.0441 (0.1020) | 0.0347 (0.0862) | 0.0884 (0.2423) | 0.0584 (0.1519) | 0.0809 (0.2016) | 0.0298 (0.0638) | 0.0709 (0.1881) |
| Final $R_1$ ($wR_2$) [all data] | 0.0554 (0.0965) | 0.0251 (0.0639) | 0.0854 (0.2015) | 0.0636 (0.1656) | 0.0514 (0.1308) | 0.0607 (0.1092) | 0.0430 (0.0922) | 0.1056 (0.2636) | 0.0773 (0.1733) | 0.1003 (0.2277) | 0.0357 (0.0657) | 0.0724 (0.1975) |
| Abs. correction | integration | integration | integration | integration | integration | integration | integration | integration | integration | integration | integration | integration |
| $T_{min}/T_{max}$ | 0.9595/0.9912 | 0.9071/0.9765 | 0.9685/0.9949 | 0.8472/0.9420 | 0.6364/0.8411 | 0.8217/0.9699 | 0.6176/0.8240 | 0.7717/0.9602 | 0.7309/0.9447 | 0.7481/0.8406 | 0.6168/0.8909 | 0.8660/0.9702 |
| Gof on $F^2$ | 1.017 | 1.056 | 1.060 | 1.088 | 1.046 | 1.036 | 1.027 | 1.101 | 1.101 | 1.100 | 1.036 | 1.068 |
| CCDC number | 1558100 | 1558101 | 1558102 | 1558103 | 1558104 | 1558105 | 1558106 | 1558107 | 1558108 | 1558109 | 1558110 | 1558111 |

**Table S2.** Absolute energy and Cartesian coordinates (Å) for the minimum structure of **6**.

E(BP86/def2-SVP) = -650.918215 a.u.

| | | | |
|---|---|---|---|
| C | -4.660469 | 0.465659 | 7.937394 |
| N | -3.625286 | 0.401085 | 8.980282 |
| C | -3.538653 | 1.638722 | 9.522881 |
| N | -4.414668 | 2.424915 | 8.880850 |
| N | -5.111141 | 1.763501 | 7.913318 |
| C | -2.801037 | -0.720100 | 9.350632 |
| C | -4.697040 | 3.807805 | 9.166298 |
| N | -4.965336 | -0.594035 | 7.257957 |
| C | -5.903369 | -0.654745 | 6.167082 |
| H | -2.946719 | 1.918577 | 10.398441 |
| C | -5.972344 | -2.012909 | 5.663959 |
| C | -7.213822 | -0.244810 | 6.633094 |
| C | -5.468490 | 0.232351 | 5.105744 |
| H | -7.923209 | -0.290722 | 5.808121 |
| H | -7.540431 | -0.911050 | 7.430196 |
| H | -7.162019 | 0.775218 | 7.010958 |
| H | -6.177877 | 0.186439 | 4.280770 |
| H | -5.416687 | 1.252379 | 5.483607 |
| H | -4.484295 | -0.075524 | 4.755753 |
| H | -6.681732 | -2.058821 | 4.838985 |
| H | -4.988149 | -2.320785 | 5.313967 |
| H | -6.298954 | -2.679149 | 6.461060 |
| H | -3.083098 | -1.589326 | 8.758341 |
| H | -1.755360 | -0.478654 | 9.165742 |
| H | -2.941315 | -0.940215 | 10.407888 |
| C | -5.705343 | 4.295312 | 8.245341 |
| C | -5.184686 | 3.930806 | 10.526287 |
| C | -3.485424 | 4.589792 | 9.014695 |
| H | -5.918887 | 5.341123 | 8.461211 |
| H | -5.339104 | 4.202934 | 7.223942 |
| H | -6.615309 | 3.708013 | 8.359200 |
| H | -5.398230 | 4.976617 | 10.742157 |
| H | -6.094652 | 3.343507 | 10.640146 |
| H | -4.427416 | 3.564672 | 11.217958 |
| H | -3.698968 | 5.635602 | 9.230565 |
| H | -2.728154 | 4.223657 | 9.706366 |
| H | -3.119185 | 4.497414 | 7.993296 |

**Table S3.** Absolute energy and Cartesian coordinates (Å) for the minimum structure of **6'**.

E(BP86/def2-SVP) = -650.911770 a.u.

| | | | |
|---|---|---|---|
| C | -4.592134 | 0.526051 | 8.006838 |
| N | -3.595388 | 0.465005 | 9.004936 |
| C | -3.453268 | 1.702220 | 9.609040 |
| N | -4.397342 | 2.419489 | 8.947966 |
| N | -5.111994 | 1.733750 | 7.958336 |
| C | -2.797617 | -0.684890 | 9.343907 |
| C | -4.711355 | 3.804160 | 9.188135 |
| N | -4.890736 | -0.553083 | 7.214733 |
| C | -5.862571 | -0.672968 | 6.158909 |
| H | -4.296043 | -1.371211 | 7.368457 |
| C | -5.814242 | -2.013115 | 5.607393 |
| C | -7.187229 | -0.416284 | 6.689846 |
| C | -5.564825 | 0.289778 | 5.116331 |
| H | -6.299775 | 0.199115 | 4.317864 |
| H | -5.601121 | 1.296275 | 5.530539 |
| H | -4.569961 | 0.097000 | 4.717579 |
| H | -7.922179 | -0.506946 | 5.891379 |
| H | -7.410846 | -1.139339 | 7.472857 |
| H | -7.223525 | 0.590213 | 7.104054 |
| H | -6.549192 | -2.103778 | 4.808925 |
| H | -4.819379 | -2.205893 | 5.208640 |
| H | -6.037860 | -2.736170 | 6.390404 |
| H | -3.101823 | -1.531452 | 8.730138 |
| H | -1.746821 | -0.463952 | 9.162423 |
| H | -2.940891 | -0.928876 | 10.395508 |
| C | -5.770910 | 4.222156 | 8.290848 |
| C | -5.147266 | 3.969813 | 10.561103 |
| C | -3.532084 | 4.614799 | 8.954290 |
| H | -6.008382 | 5.269313 | 8.472476 |
| H | -5.443526 | 4.097745 | 7.259702 |
| H | -6.656583 | 3.613338 | 8.466473 |
| H | -3.769556 | 5.661957 | 9.135918 |
| H | -2.736322 | 4.300870 | 9.628184 |
| H | -3.204700 | 4.490389 | 7.923144 |
| H | -5.384738 | 5.016970 | 10.742731 |
| H | -6.032939 | 3.360995 | 10.736728 |
| H | -4.351503 | 3.655884 | 11.234996 |

**Table S4.** Experimentally determined and DFT computed bond lengths (Å) and angles (°) of **6**.

| | **XRD** | **DFT** |
|---|---|---|
| C1–N2 | 1.315(2) | 1.337 |
| C1–N3 | 1.339(2) | 1.352 |
| N2–N1 | 1.383(2) | 1.365 |
| C2–N4 | 1.308(2) | 1.292 |
| C2–N3 | 1.420(2) | 1.453 |
| C2–N1 | 1.364(2) | 1.385 |
| N1–C1–N3 | 107.46(13) | 107.30 |

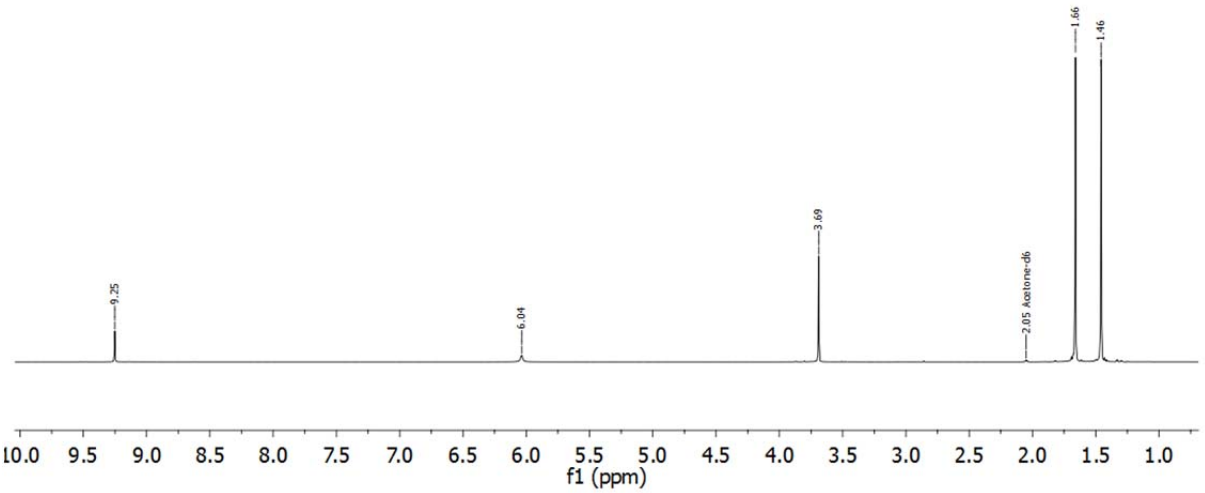


**Figure S1.** $^{1}$H NMR spectrum of **6**H[$BF_4$] (acetone-$d_6$, 400 MHz).

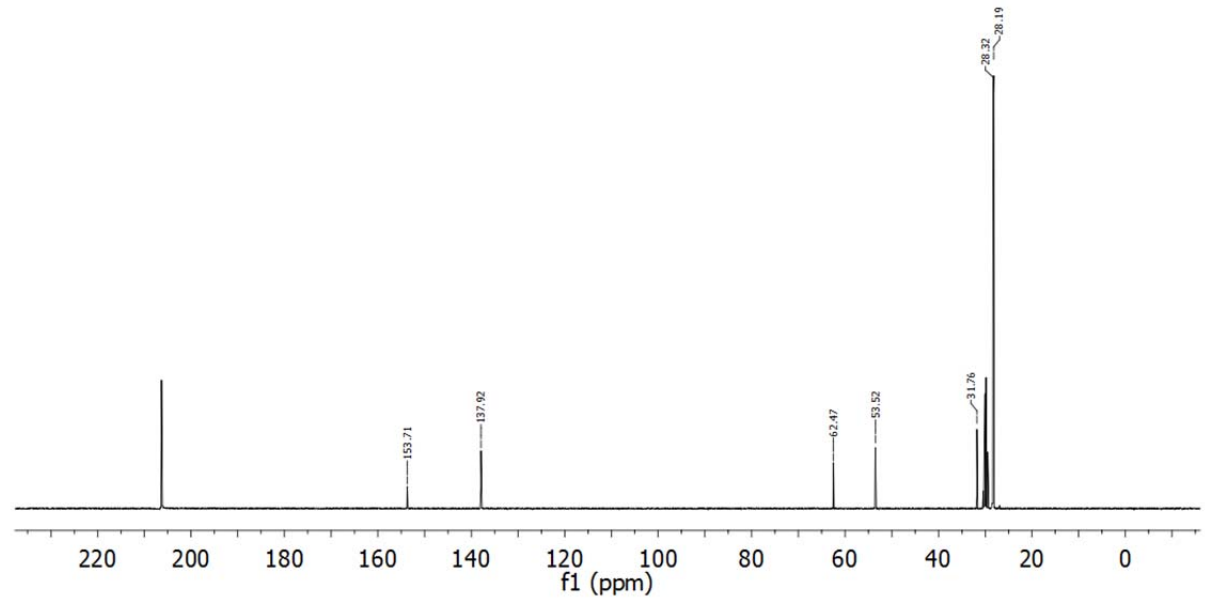


**Figure S2.** $^{13}$C NMR spectrum of **6**H[$BF_4$] (acetone-$d_6$, 100 MHz).

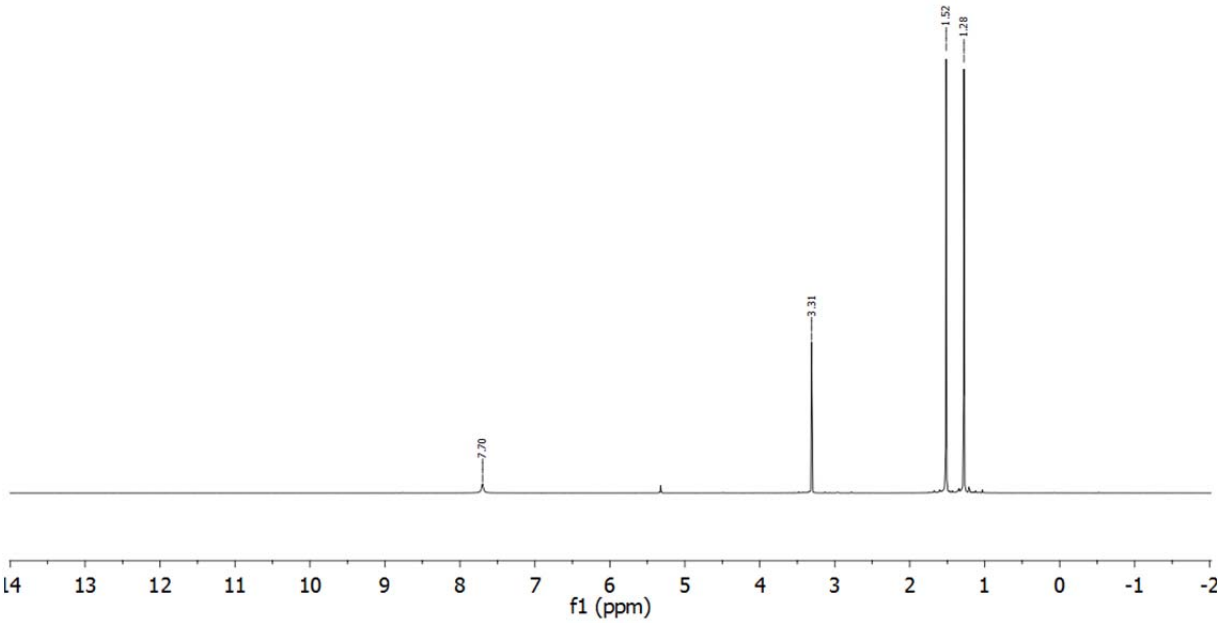


**Figure S3.** $^{1}$H NMR spectrum of **6** ($CD_2Cl_2$, 400 MHz).

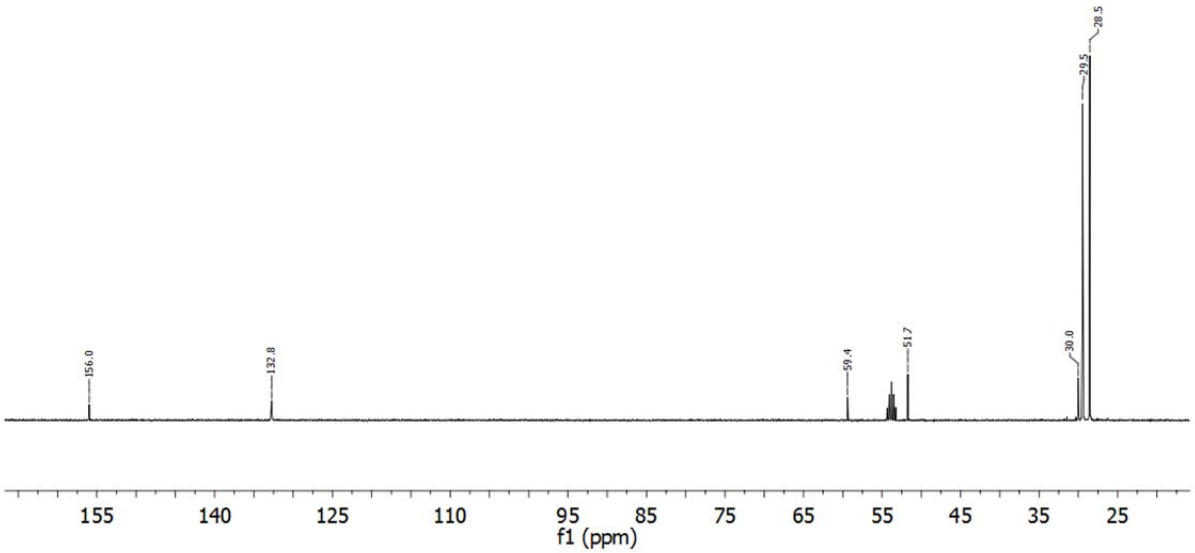


**Figure S4.** $^{13}$C NMR spectrum of **6** ($CD_2Cl_2$, 100 MHz).

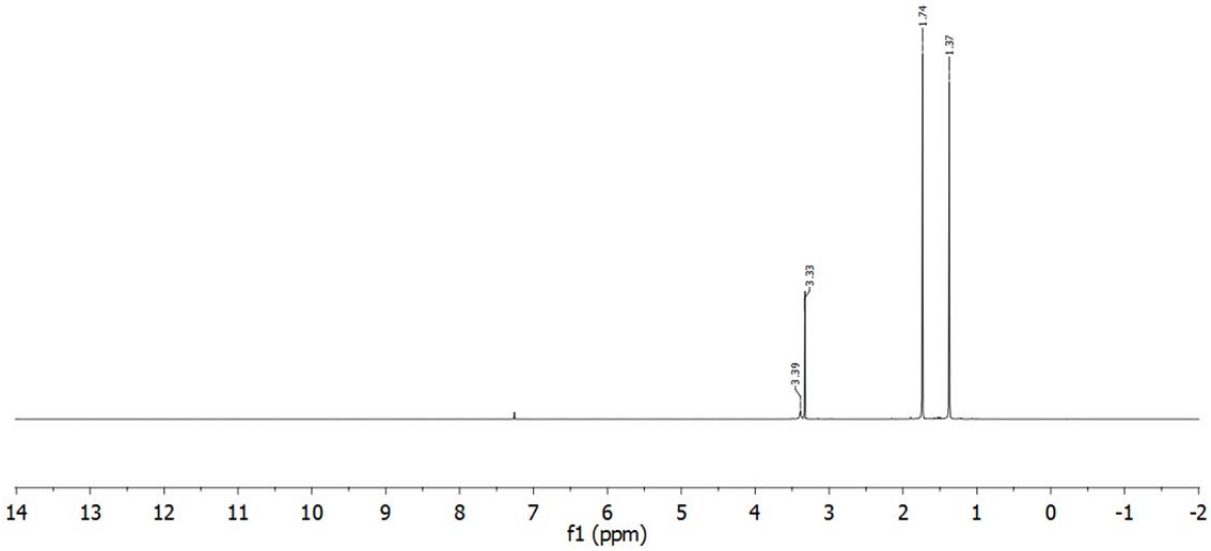


**Figure S5.** $^{1}$H NMR spectrum of **6'**=S ($CDCl_3$, 400 MHz).

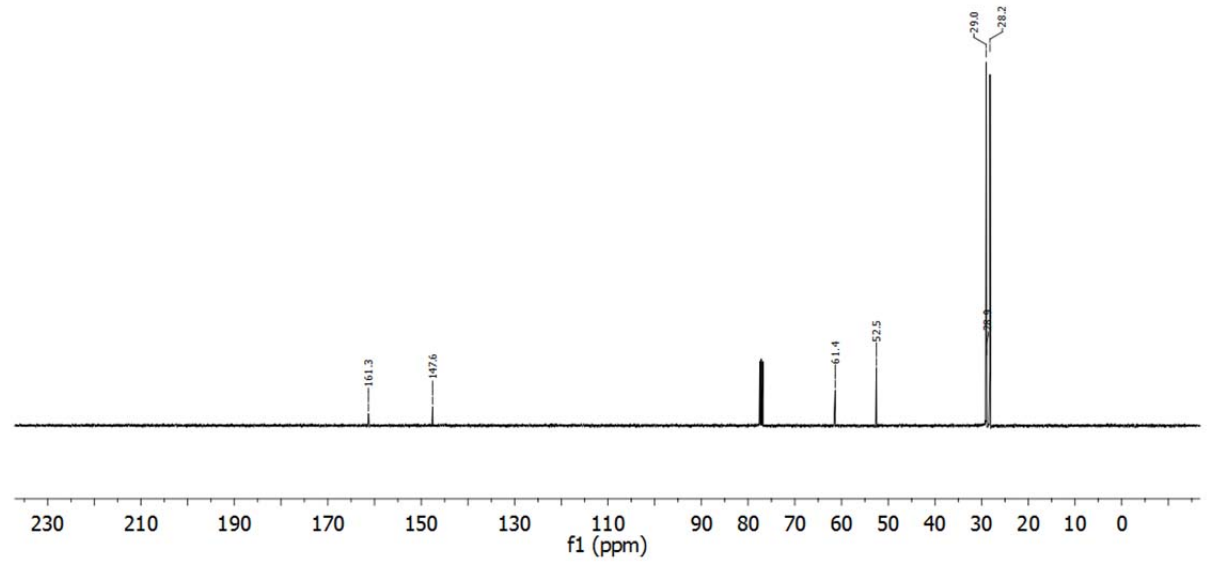


**Figure S6.** $^{13}$C NMR spectrum of **6'**=S ($CDCl_3$, 100 MHz).

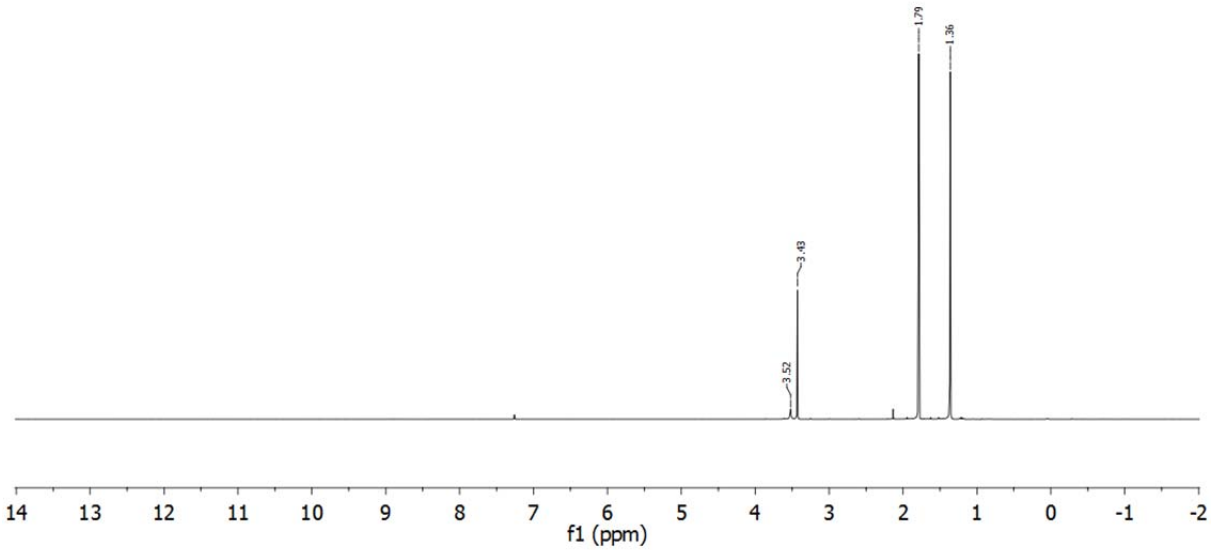


**Figure S7.** $^{1}$H NMR spectrum of **6'**=Se ($CDCl_3$, 400 MHz). The signal at 2.1 ppm is due to acetone.

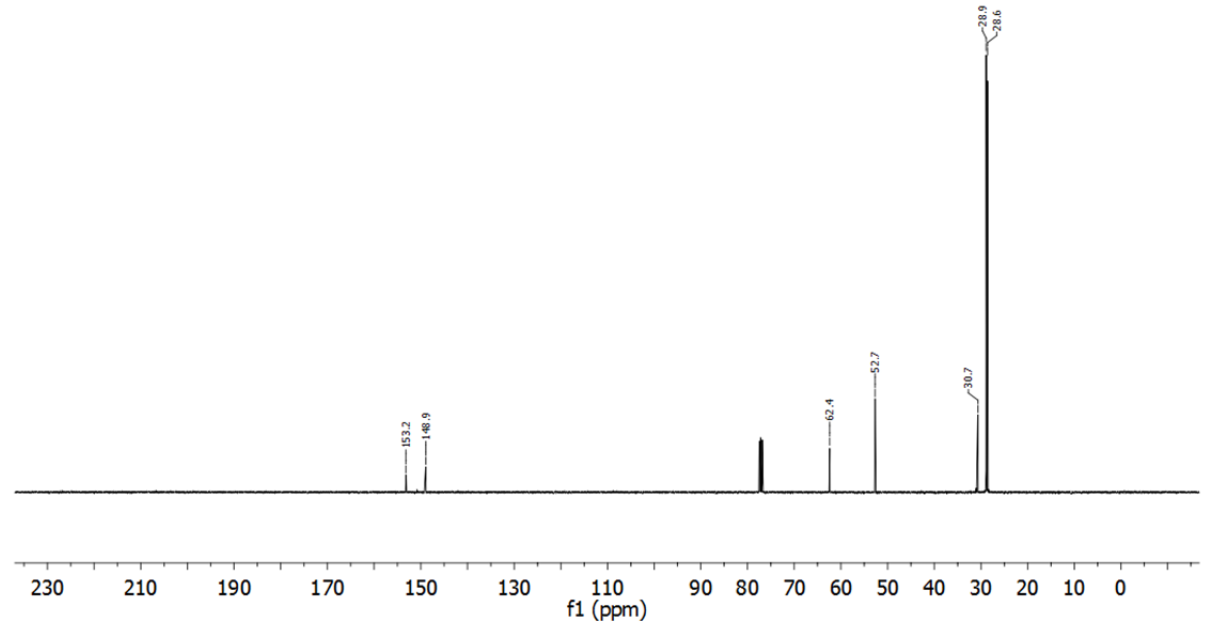


**Figure S8.** $^{13}$C NMR spectrum of **6'**=Se ($CDCl_3$, 100 MHz).

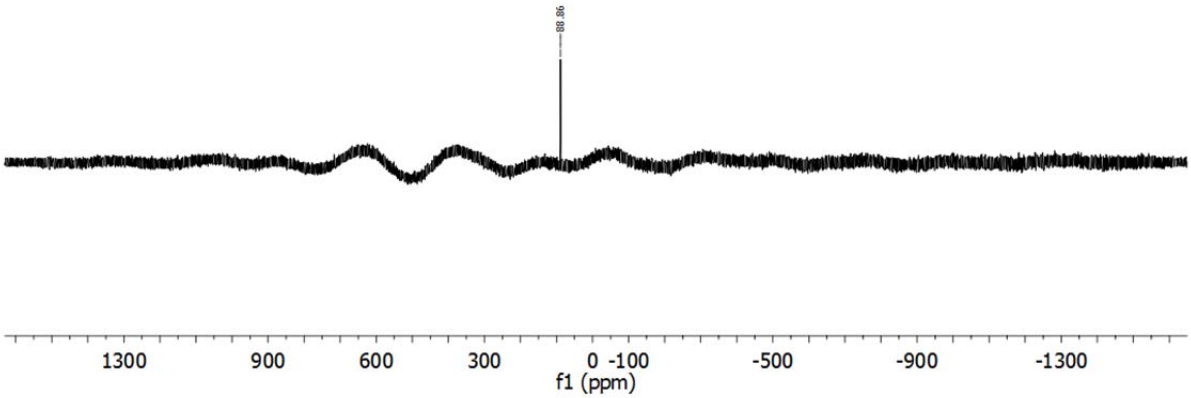


**Figure S9.** $^{77}$Se NMR spectrum of **6'**=Se ($CDCl_3$, 95 MHz).

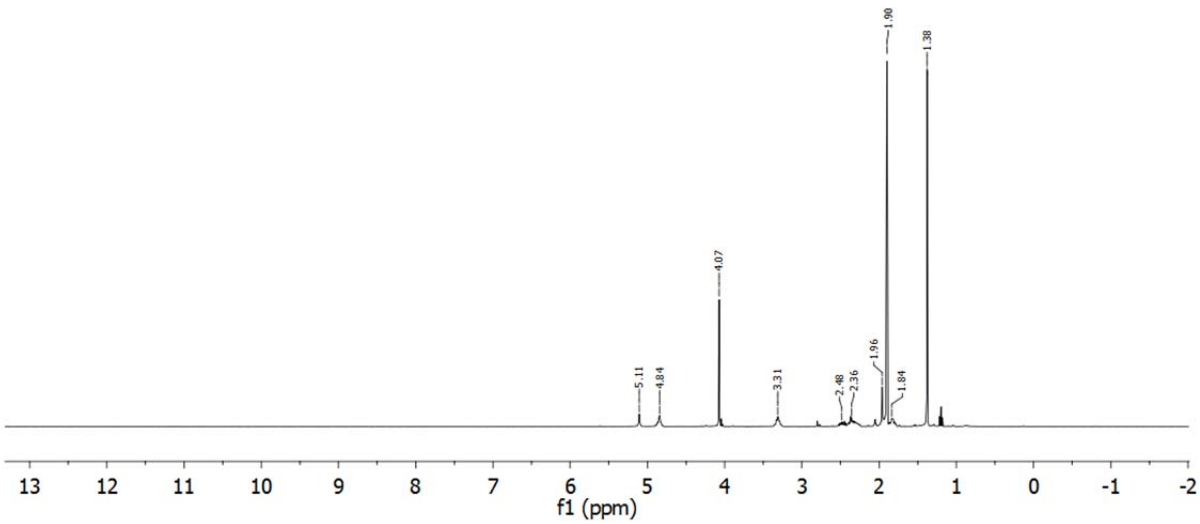


**Figure S10.** $^{1}$H NMR spectrum [RhCl(**6'**)(COD)] (acetone-$d_6$, 400 MHz). The minor signals at 1.1 ppm and 2.7 ppm are due to an unknown impurity.

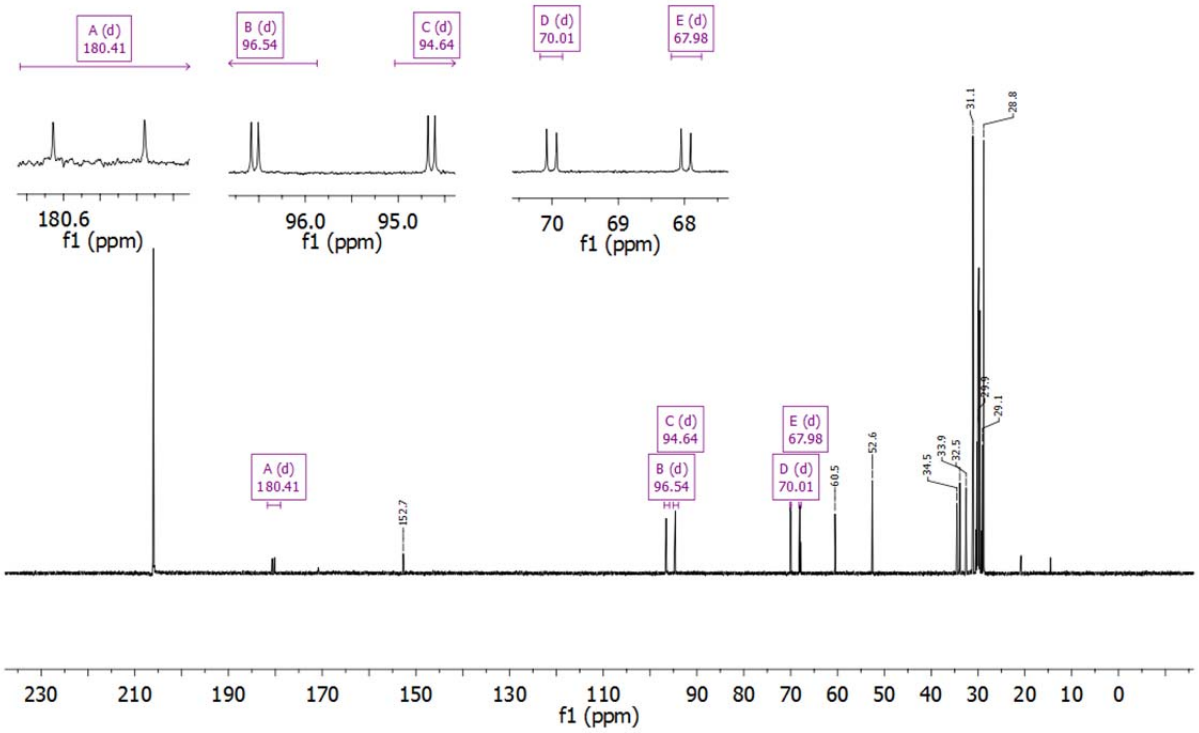


**Figure S11.** $^{13}$C NMR spectrum of [RhCl(**6')**(COD)] (acetone-$d_6$, 100 MHz). The minor signals at 21 and 15 ppm are due to an unknown impurity.

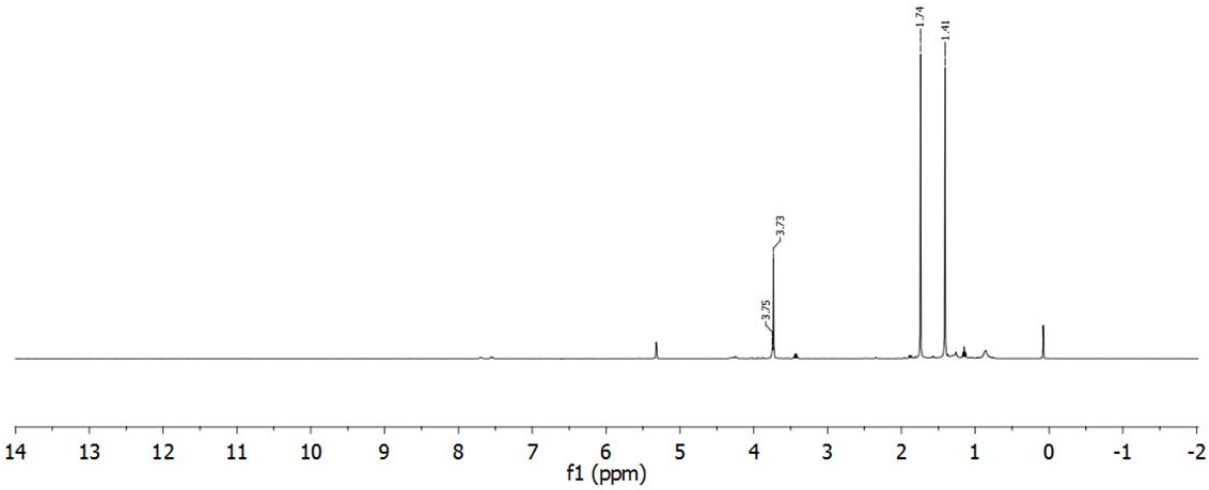


**Figure S12.** $^{1}$H NMR spectrum of [RhCl(**6')**$(CO)_2$] ($CD_2Cl_2$, 400 MHz). The signal at 0.1 ppm is due to silicon grease. The minor signals 7.5, 3.4, 1.3 and 0.8 ppm are due to unknown impurities.

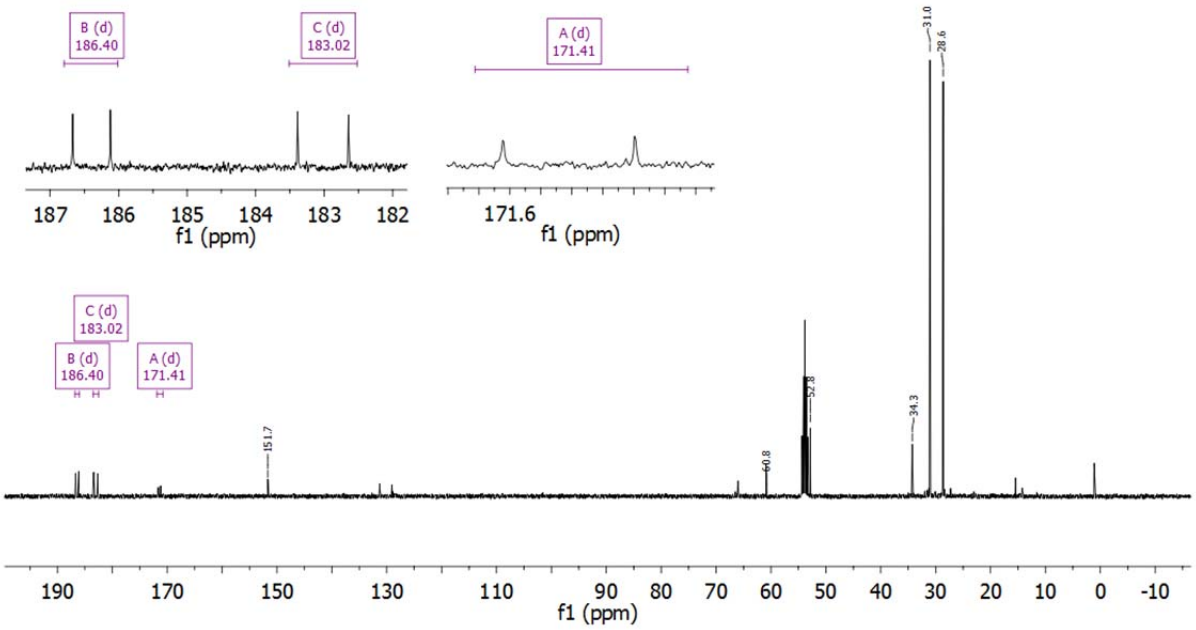


**Figure S13.** $^{13}C$ NMR spectrum of [RhCl(**6'**)$(CO)_2$] ($CD_2Cl_2$, 100 MHz). The signal at 1 ppm is due to silicon grease. The minor signals at 133, 128, 65 and 15 ppm are due to unknown impurities.

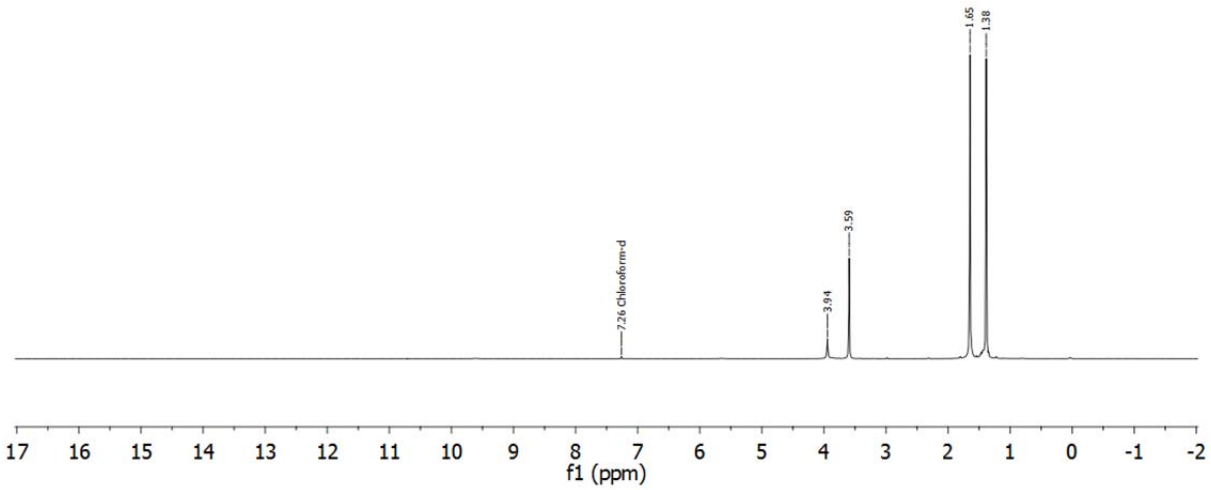


**Figure S14.** $^{1}H$ NMR spectrum of [CuCl(**6'**)] ($CDCl_3$, 400 MHz).

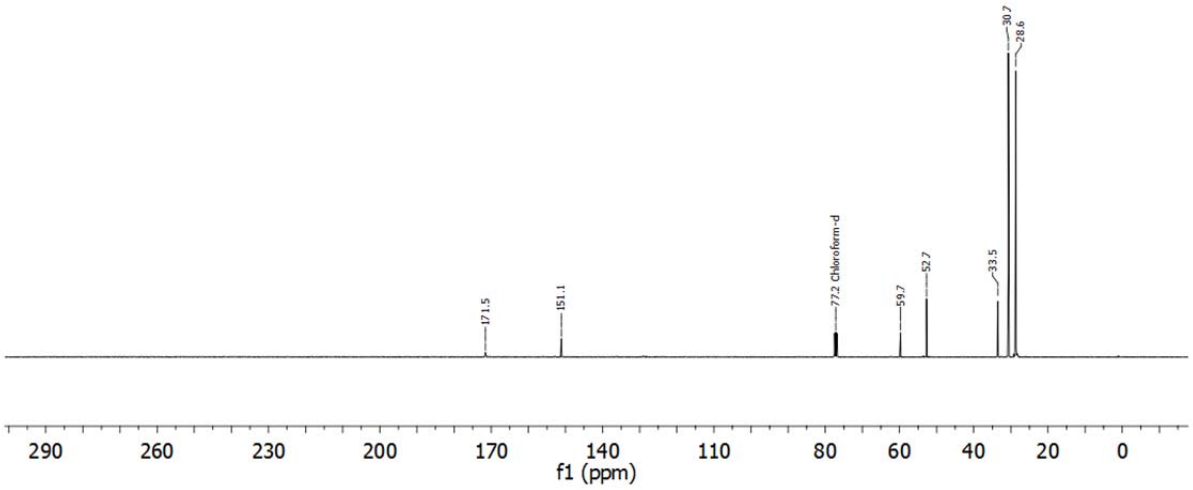


**Figure S15.** $^{13}C$ NMR spectrum of [CuCl(**6'**)] ($CDCl_3$, 100 MHz).

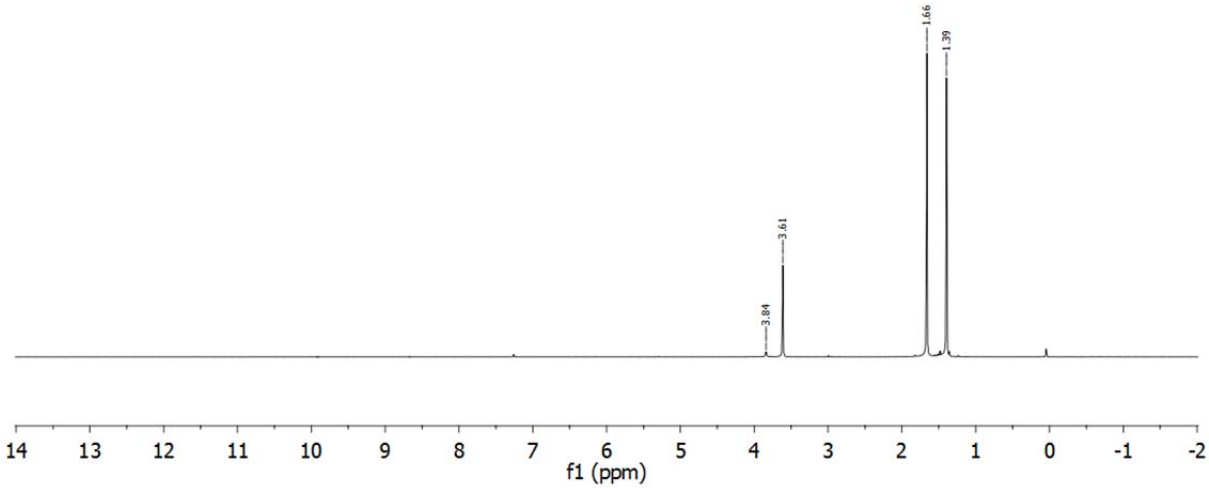


**Figure S16.** $^{1}H$ NMR spectrum of [CuBr(**6'**)] ($CDCl_3$, 400 MHz). The signal at 0.1 ppm is due to silicon grease.

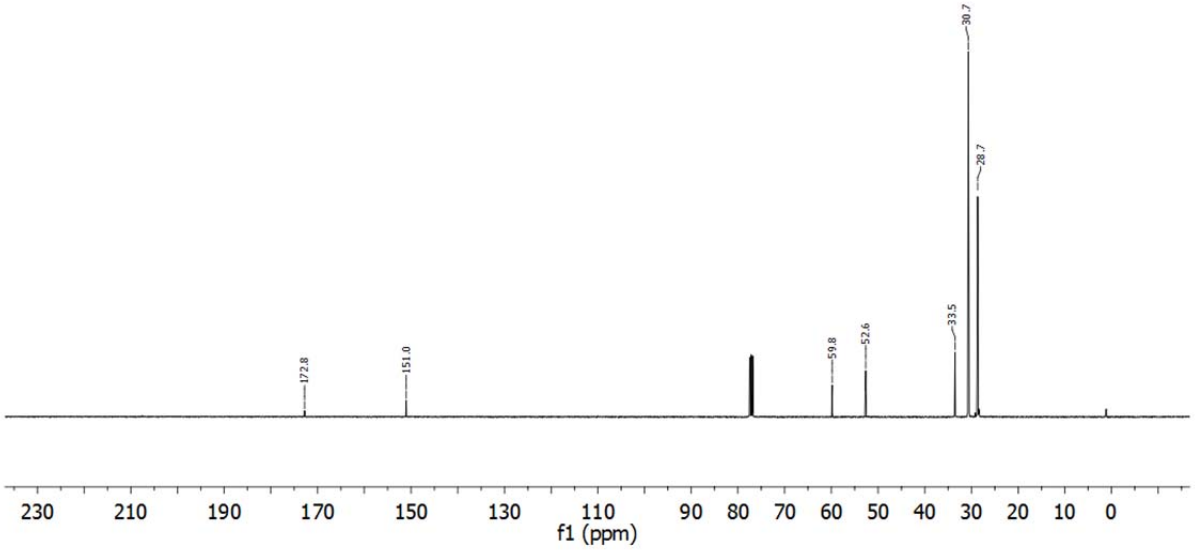


**Figure S17.** $^{13}C$ NMR spectrum of [CuBr(**6'**)] ($CDCl_3$, 100 MHz). The signal at 1 ppm is due to silicon grease.

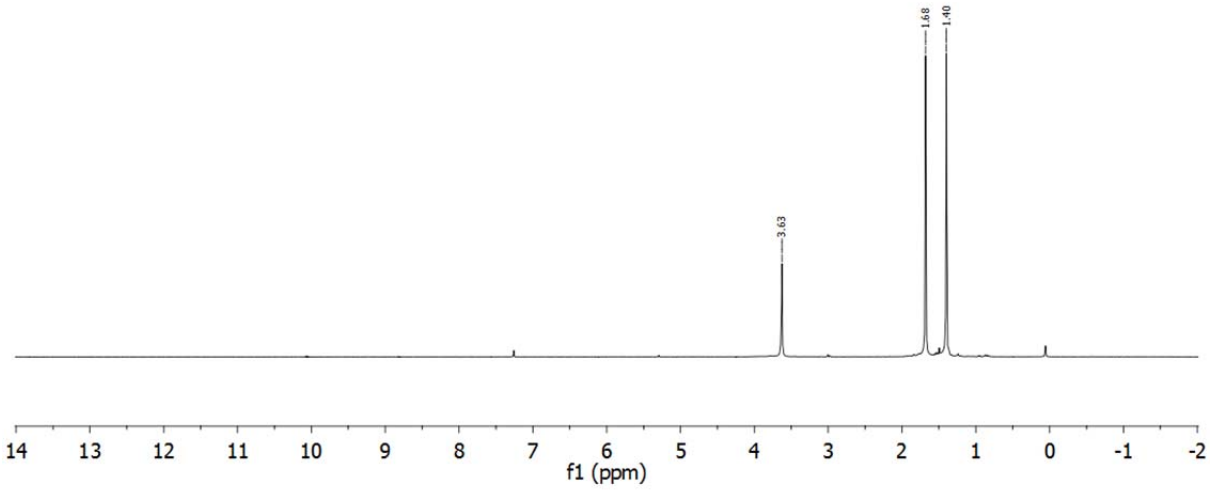


**Figure S18.** $^{1}H$ NMR spectrum of [CuI(**6'**)] ($CDCl_3$, 400 MHz). The signal at 0.1 ppm is due to silicon grease.

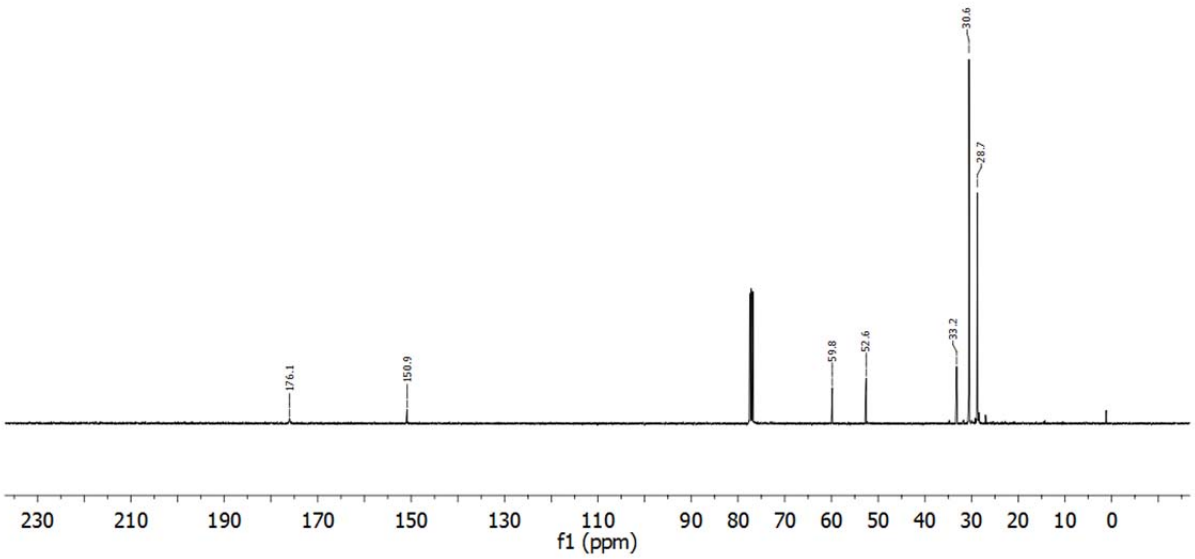


**Figure S19.** $^{13}$C NMR spectrum of [CuI(**6'**)] ($CDCl_3$, 100 MHz). The signal at 1 ppm is due to silicon grease.

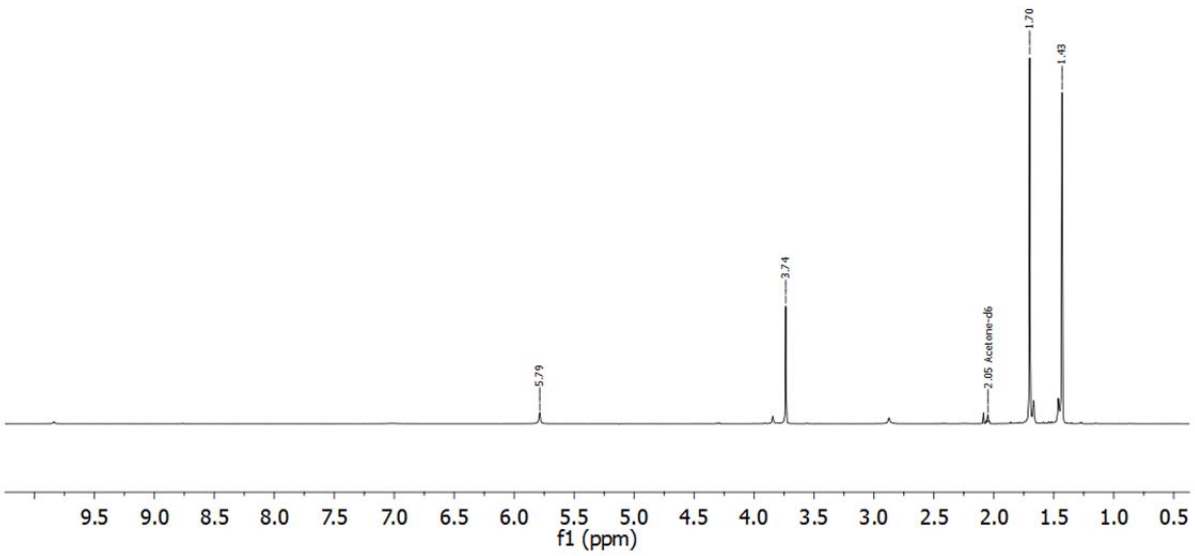


**Figure S20.** $^{1}$H NMR spectrum of [AgCl(**6'**)] (acetone-$d_6$, 400 MHz). The signal at 2.85 ppm is due to water. The minor signals at 3.84, 1.67 and 1.46 ppm are due to **6**H$^+$. The signal at 2.07 ppm is due to an unknown impurity.

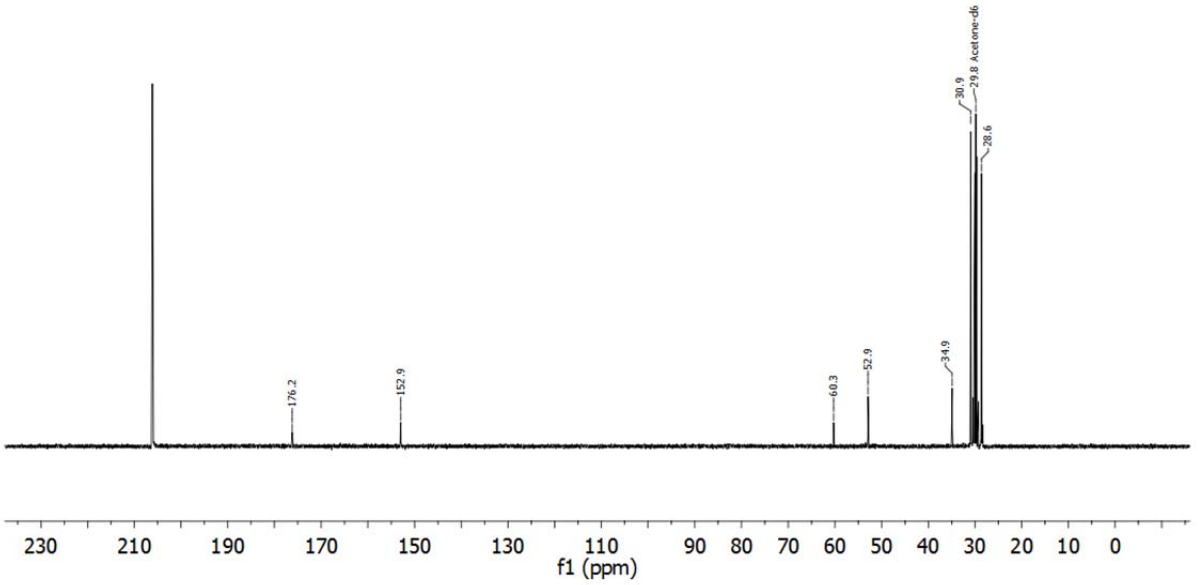


**Figure S21.** $^{13}$C NMR spectrum of [AgCl(**6'**)] (acetone-$d_6$, 100 MHz).

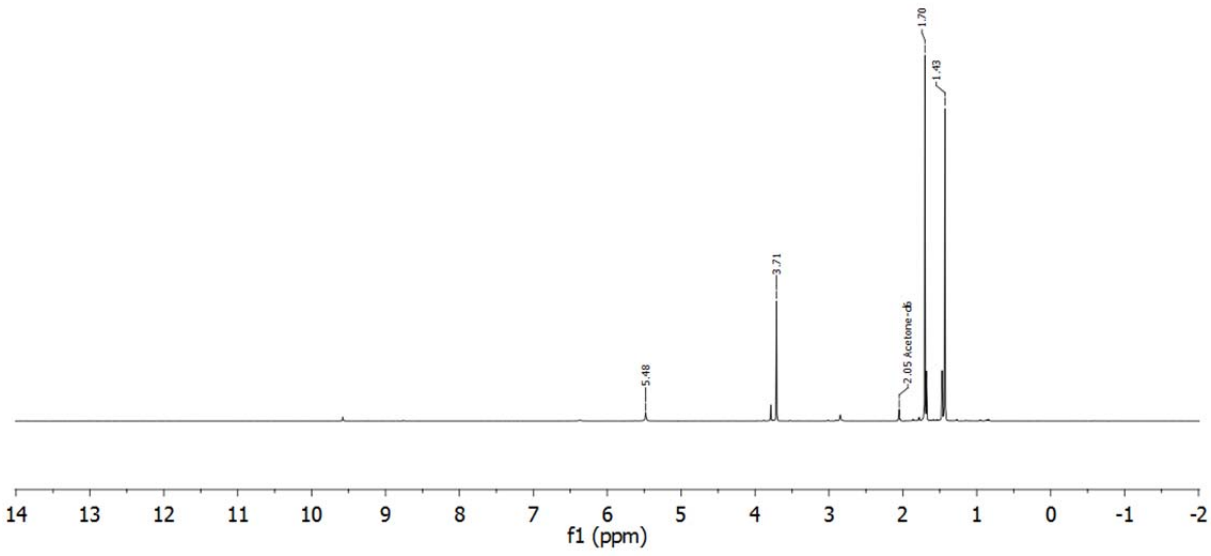


**Figure S22.** $^{1}$H NMR spectrum of [AgBr(**6'**)] (acetone-$d_6$, 400 MHz). The signal at 2.85 ppm is due to water. The minor signals at 3.80, 1.68 and 1.47 ppm are due to **6**H$^{+}$.

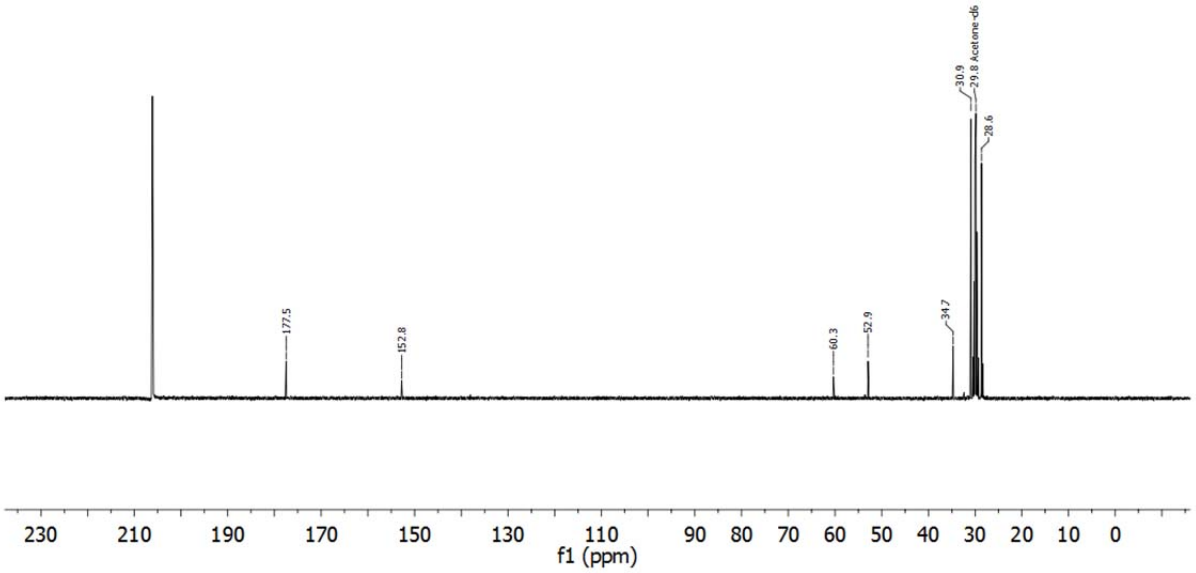


**Figure S23.** $^{13}$C NMR spectrum of [AgBr(**6'**)] (acetone-$d_6$, 100 MHz).

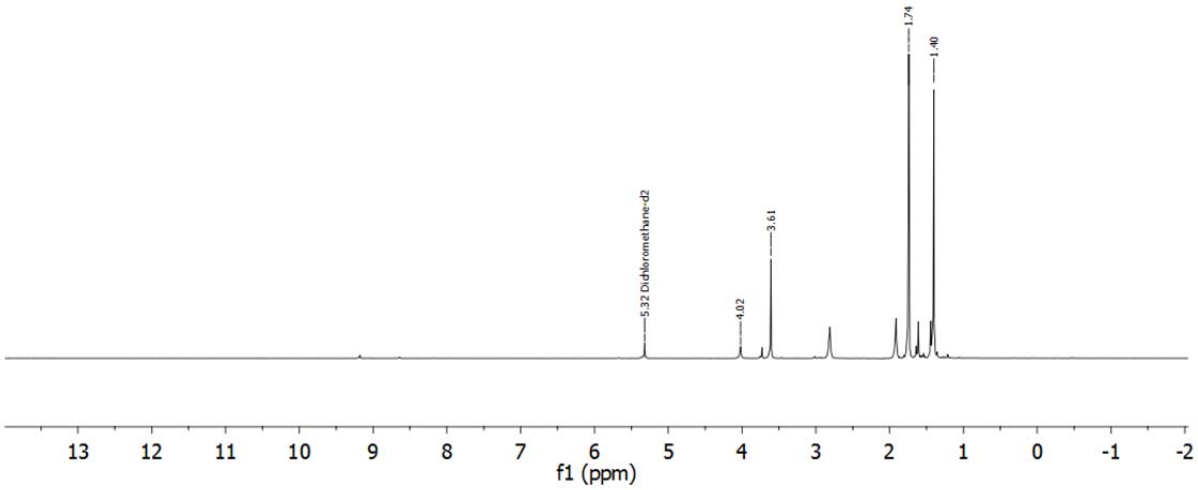


**Figure S24.** $^{1}$H NMR spectrum of [AuCl(**6'**)] ($CD_2Cl_2$, 500 MHz). The signals at 2.81 ppm and 1.91 ppm are due to residual tetrahydrothiophene. The minor signals at 3.73, 1.61 and 1.44 ppm are due to **6**H$^+$.

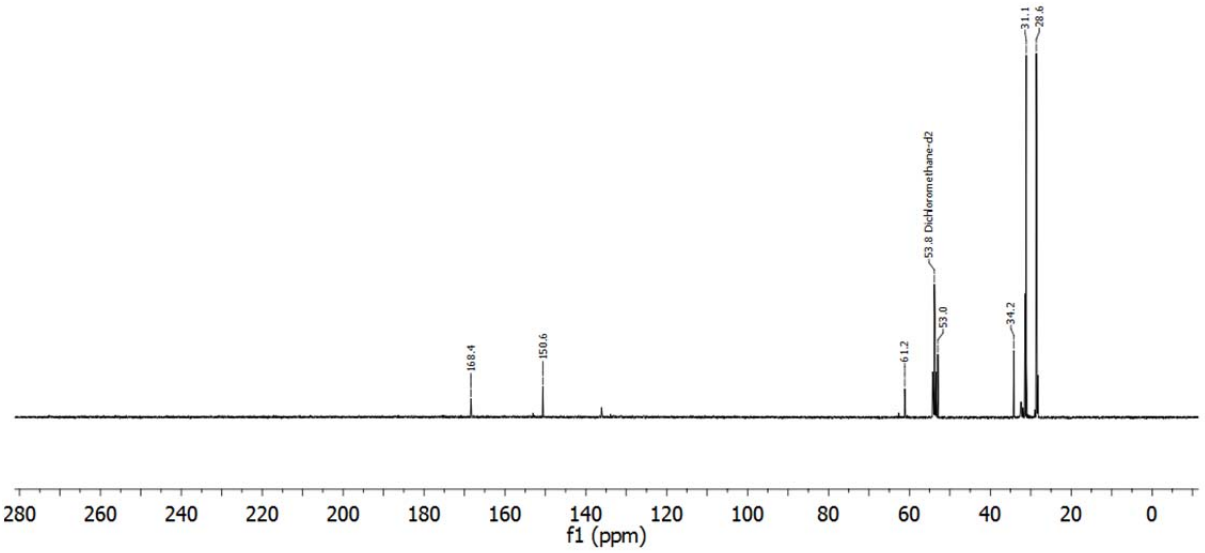


**Figure S25.** $^{13}$C NMR spectrum of [AuCl(**6'**)] ($CD_2Cl_2$, 125 MHz). The signal at 31.4 ppm is due to tetrahydrothiophene. The signals at 153.0, 136.1, 62.6, 32.4, 28.4 and 28.2 ppm are due to **6**H$^+$.

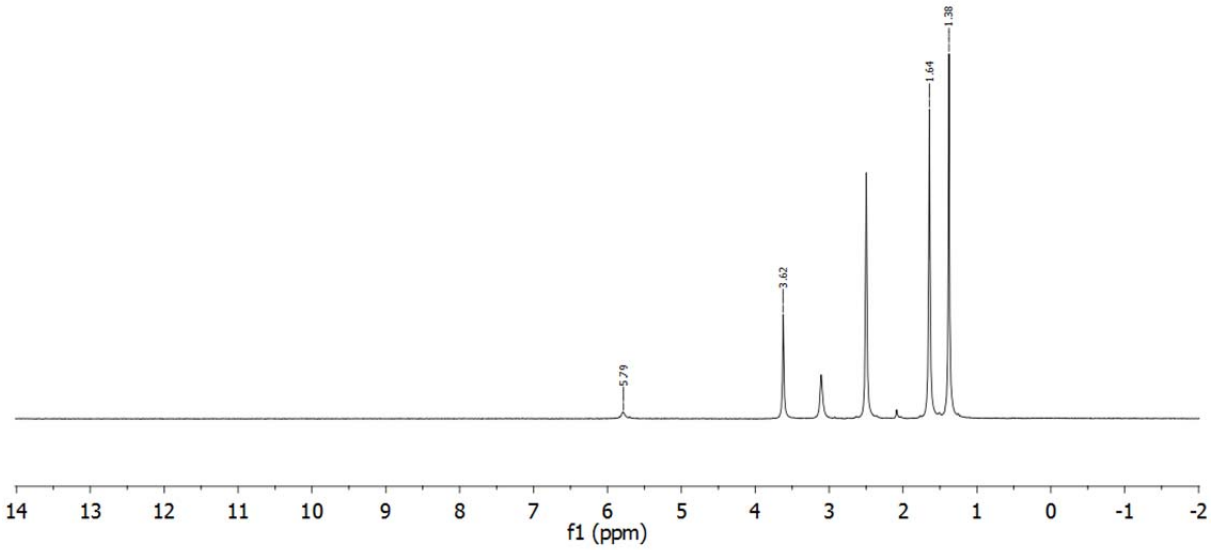


**Figure S26.** $^1$H NMR spectrum of [CuCl(**6'**)$_2$] (DMSO-$d_6$, 500 MHz, 70 °C). The signals at 3.10 and 2.05 ppm are due to water and acetone, respectively.

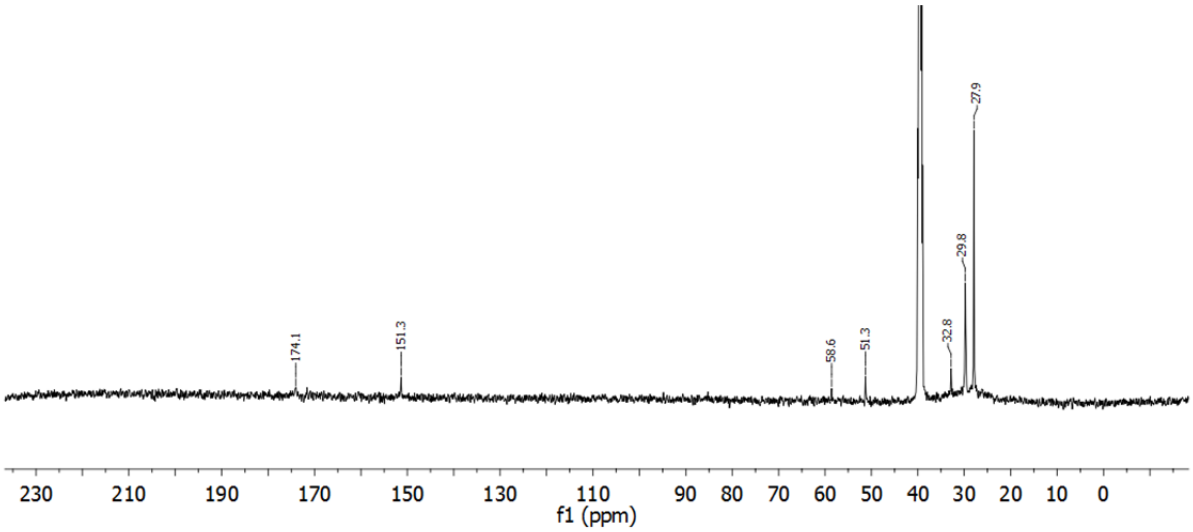


**Figure S27.** $^{13}$C NMR spectrum of [CuCl(**6'**)$_2$] (DMSO-$d_6$, 125 MHz, 70 °C).

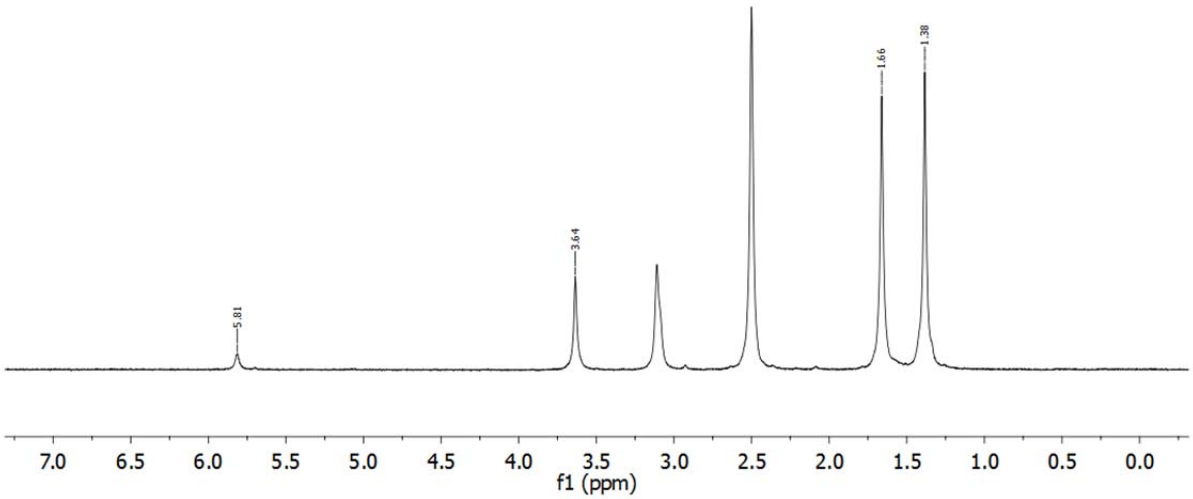


**Figure S28.** $^{1}$H NMR spectrum of [CuBr(**6'**)$_2$] (DMSO-$d_6$, 500 MHz, 70 °C). The signal at 3.10 ppm is due to water.

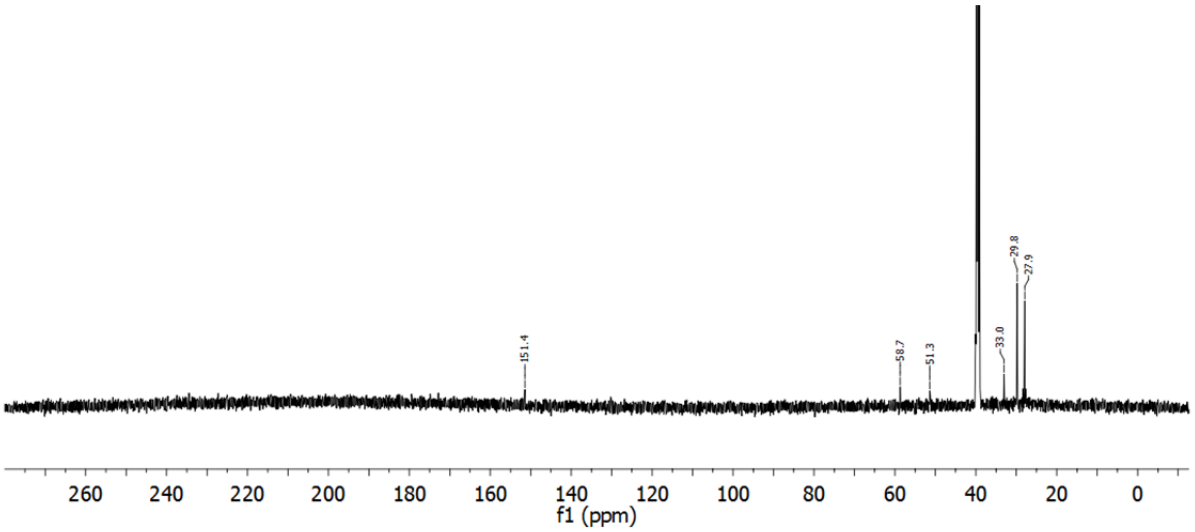


**Figure S29.** $^{13}$C NMR spectrum of [CuBr(**6'**)$_2$] (DMSO-$d_6$, 125 MHz, 70 °C).

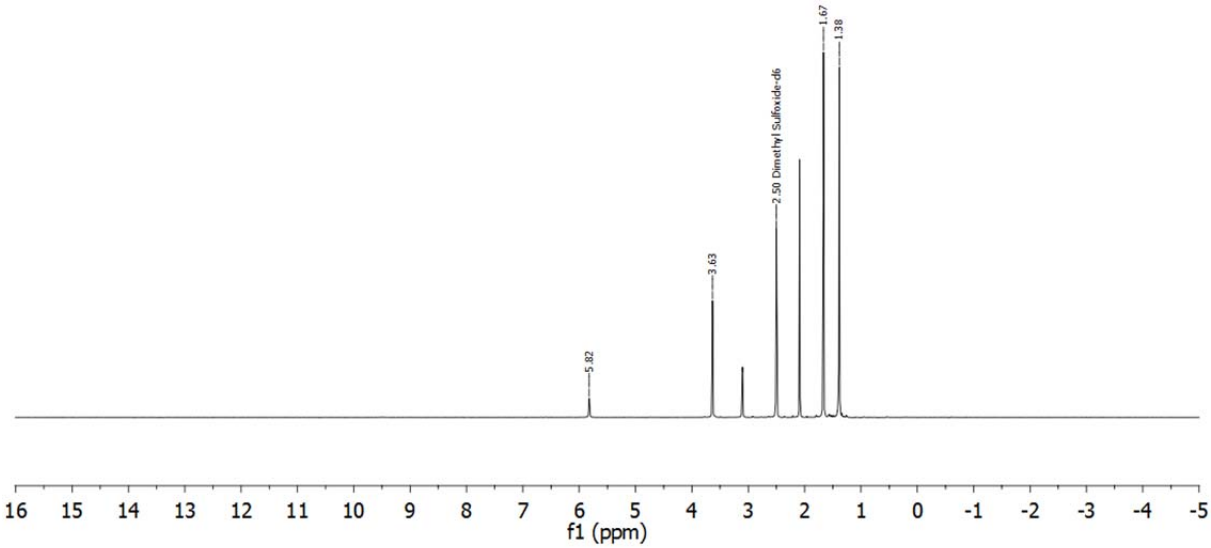


**Figure S30.** $^{1}$H NMR spectrum of [CuI(**6'**)$_2$] (DMSO-$d_6$, 500 MHz, 70 °C). The signals at 3.10 and 2.09 ppm are due to water and acetone, respectively.

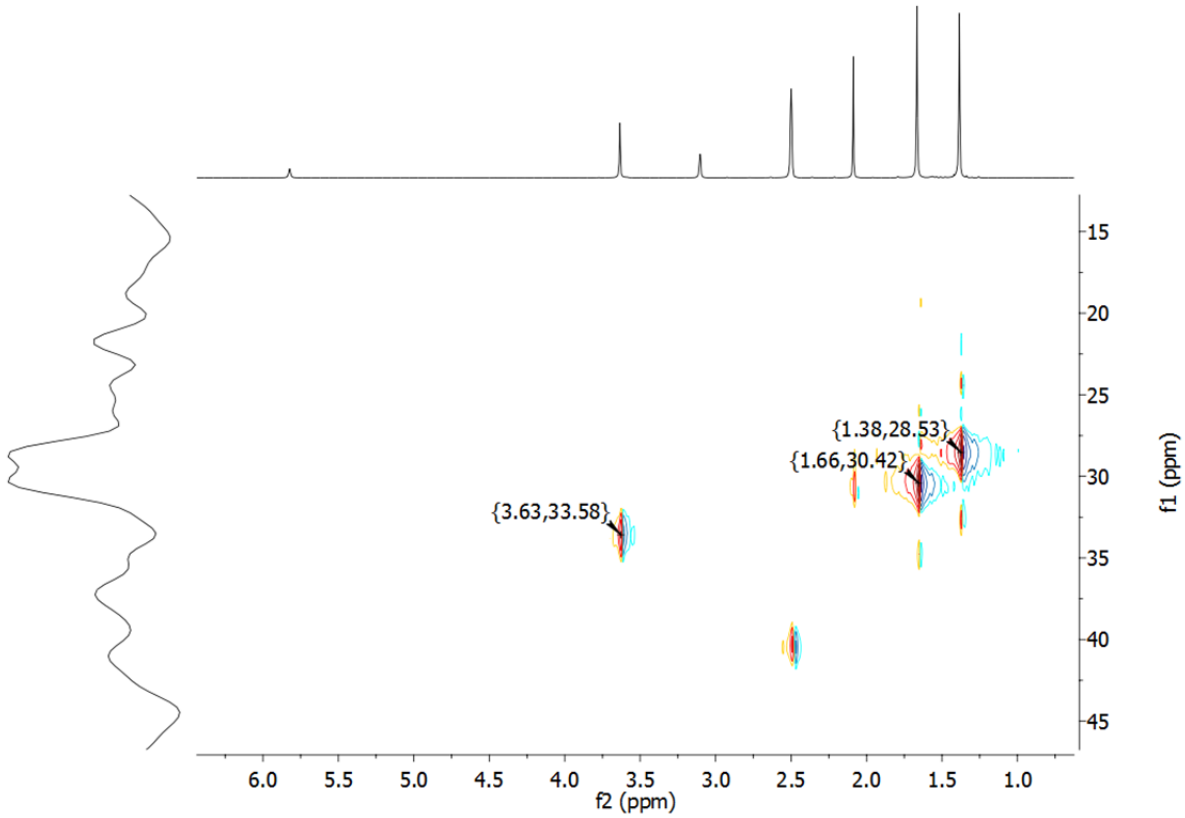


**Figure S31.** HSQC NMR spectrum of [CuI(**6'**)$_2$] (DMSO-$d_6$, 500 MHz, 70 °C).

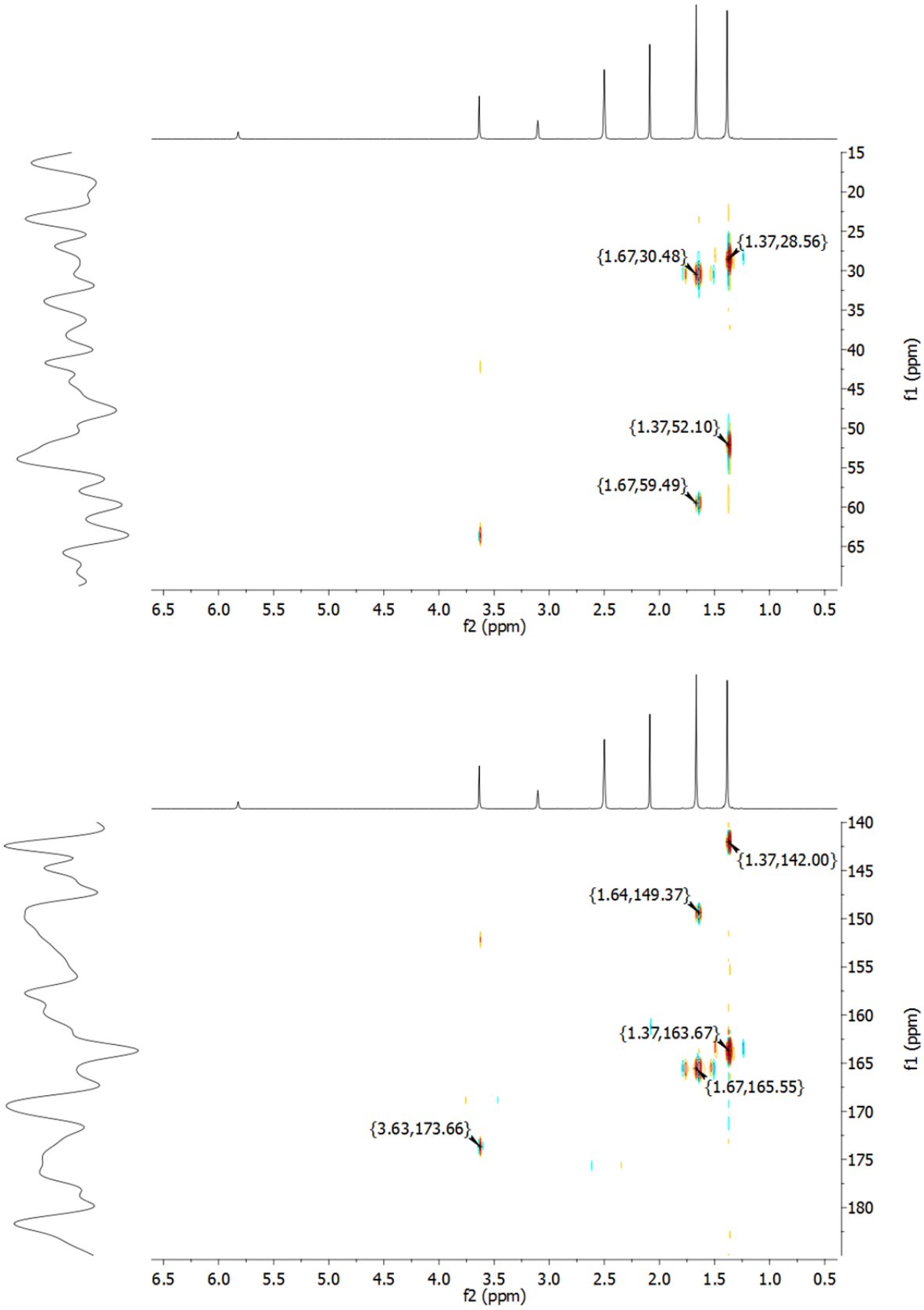


**Figure S32.** HMBC NMR spectrum of [CuI(**6'**)$_2$] (DMSO-$d_6$, 500 MHz, 70 °C), displayed in two sections.

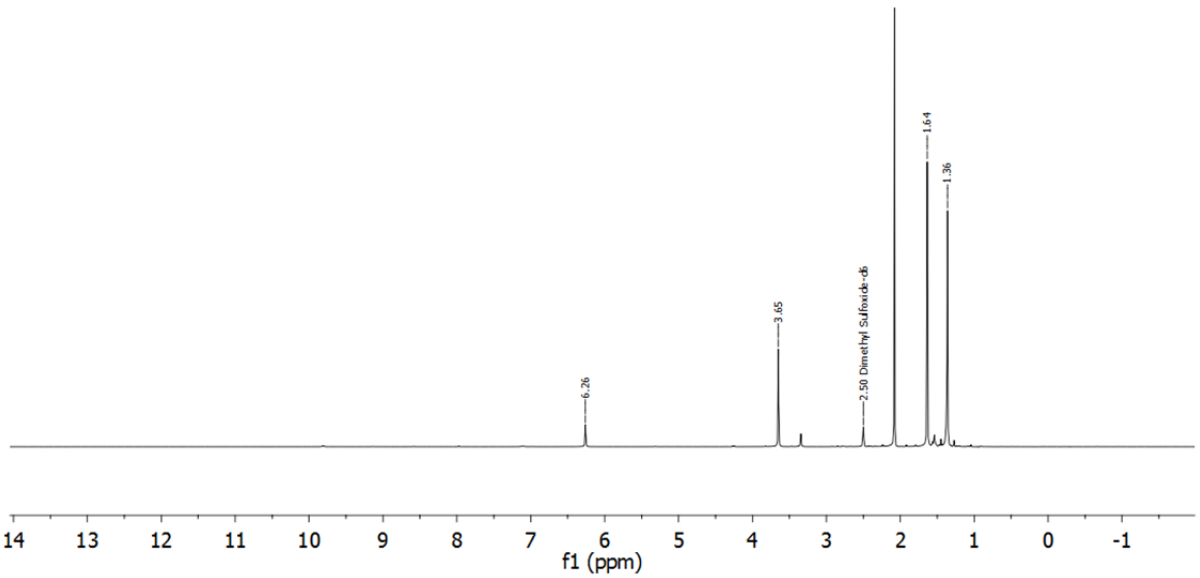


**Figure S33.** $^{1}$H NMR spectrum of [Ag(**6'**)$_2$]Cl (DMSO-$d_6$, 400 MHz). The signals at 3.33 ppm and 2.10 ppm are due to water and acetone, respectively.

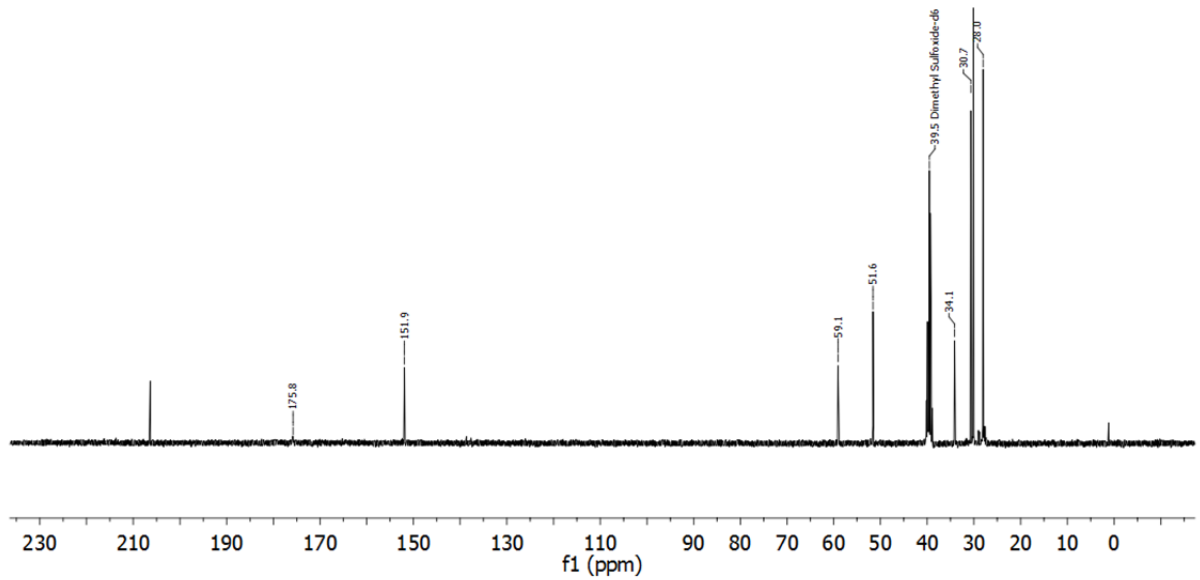


**Figure S34.** $^{13}$C NMR spectrum of [Ag(**6'**)$_2$]Cl (DMSO-d$_6$, 100 MHz). The signals at 205.9 ppm and 30.6 ppm are due to acetone.

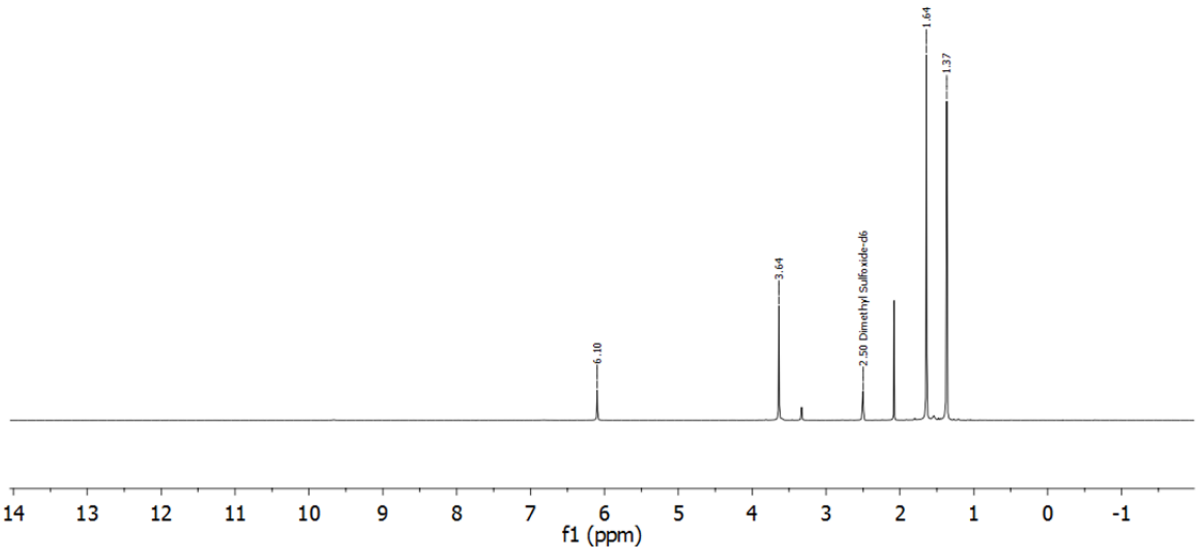


**Figure S35.** $^{1}$H NMR spectrum of [Ag(**6'**)$_2$]Br (DMSO-$d_6$, 400 MHz). The signals at 3.33 ppm and 2.10 ppm are due to water and acetone, respectively.

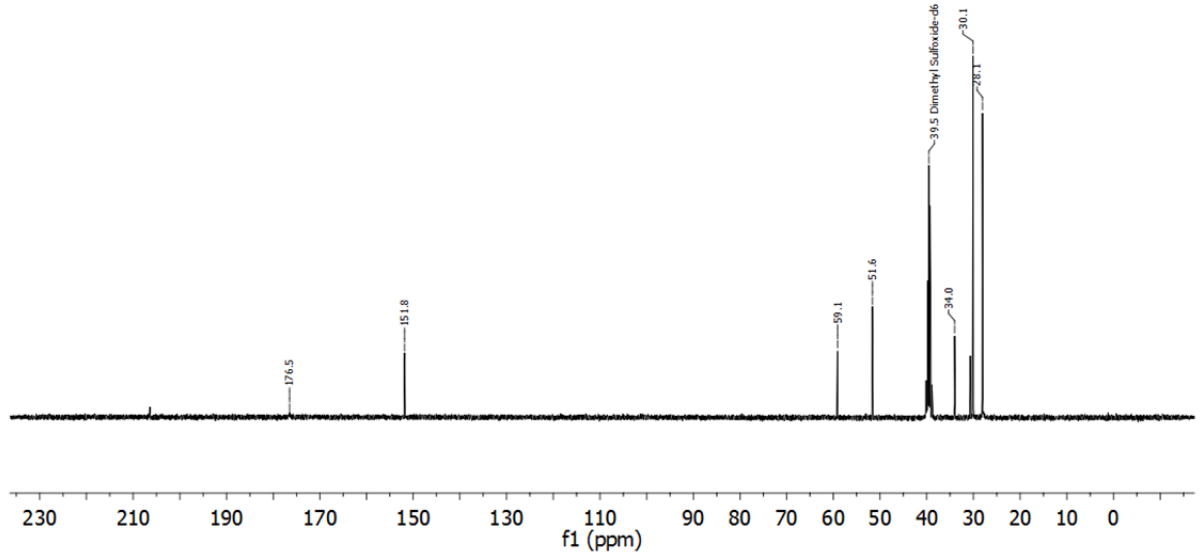


**Figure S36.** $^{13}$C NMR spectrum of [Ag(**6'**)$_2$]Br (DMSO-$d_6$, 100 MHz). The signals at 205.9 ppm and 30.6 ppm are due to acetone.

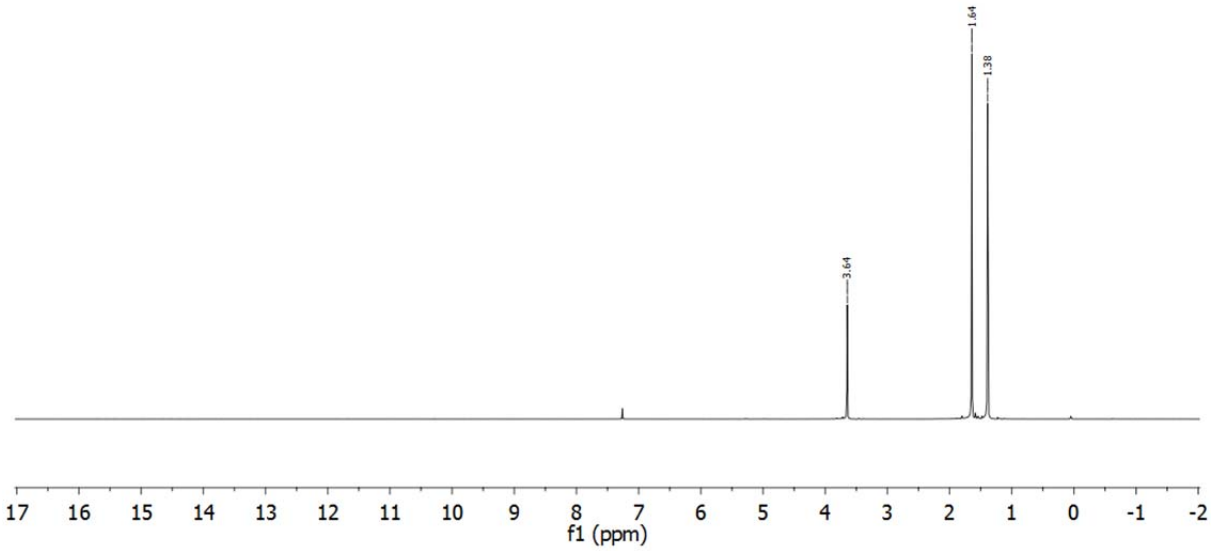


**Figure S37.** $^{1}$H NMR spectrum of [Ag(**6'**)$_2$](OTf) ($CDCl_3$, 400 MHz).

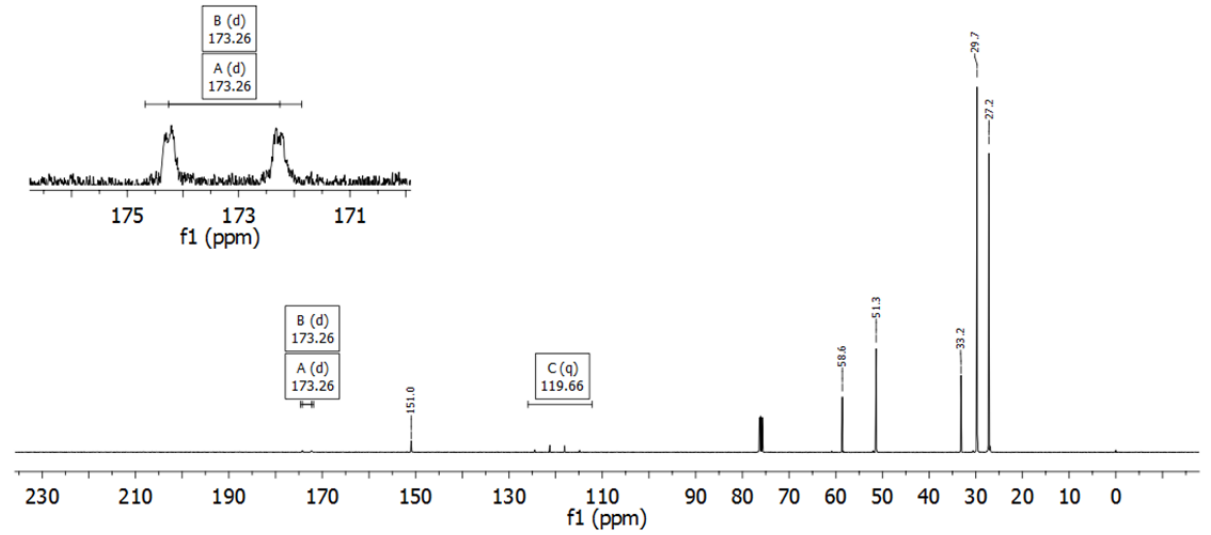


**Figure S38.** $^{13}$C NMR spectrum of [Ag(**6'**)$_2$](OTf) ($CDCl_3$, 100 MHz).

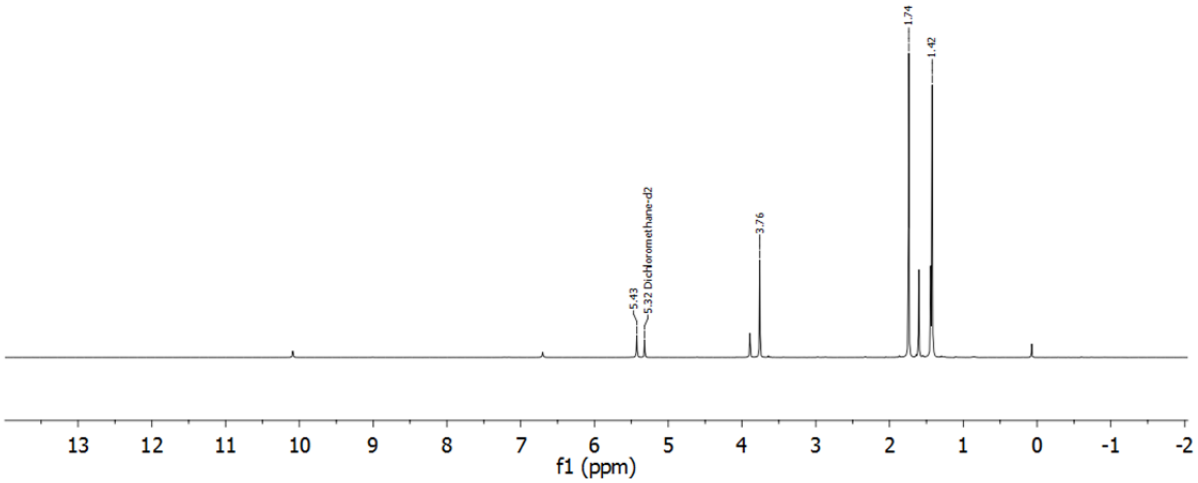


**Figure S39.** $^{1}$H NMR spectrum of [Au(**6'**)$_2$]Cl ($CD_2Cl_2$, 500 MHz). The signal at 0.1 ppm is due to silicon grease. The minor signals at 10.09, 6.70, 3.89, 1.60 and 1.44 ppm are due to **6**H$^+$.

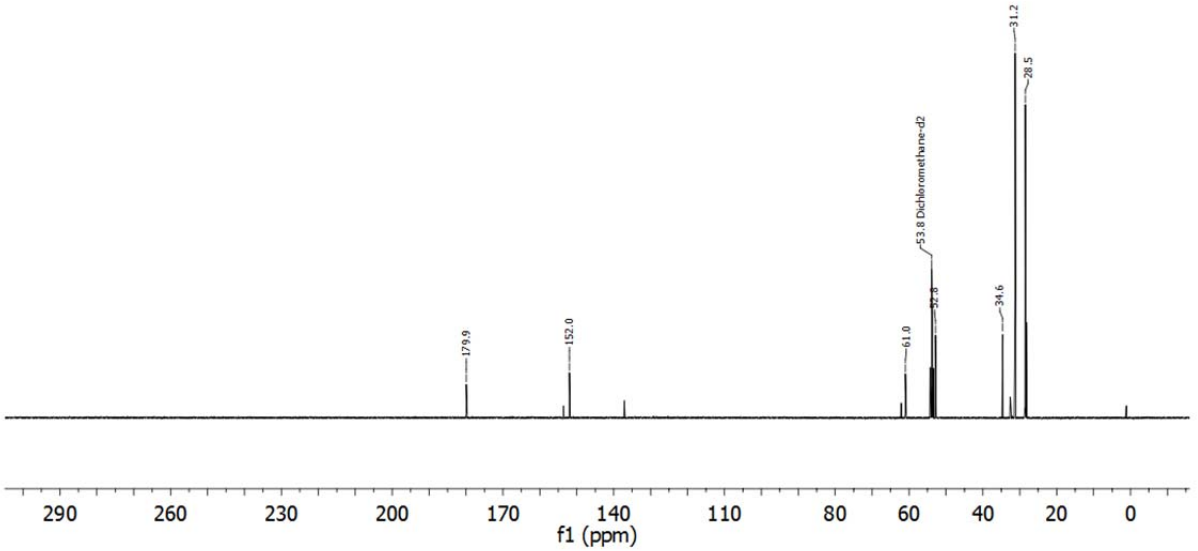


**Figure S40.** $^{13}$C NMR spectrum of [Au(**6'**)$_2$]Cl ($CD_2Cl_2$, 125 MHz). The signal at 1 ppm is due to silicon grease. The minor signals at 153.6, 137.1, 62.1, 53.4, 32.6, 28.5 and 28.2 ppm are due to **6**H$^+$.